

## Multiphoton ionization and fragmentation processes of methyl iodide clusters at 266 and 355 nm

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### Abstract

The multiphoton ionization (MPI) and dissociation dynamics of methyl iodide clusters at 266 and 355 nm are studied using a reflectron time-of-flight (RTOF) mass spectrometer. The excitation wavelengths were chosen to access the repulsive valence *A* state and the Rydberg *C* state. MPI mass spectrum at 266 nm consists mostly of fragment ions,  $\text{CH}_3^+$ ,  $\text{I}^+$ , and  $\text{I}_2^+$ . This is consistent with a ladder-switching mechanism in which rapid one-photon dissociation occurs from the repulsive potential energy surface followed by multiphoton ionization of neutral photofragments. The observation of considerable amount of parent ion and methyl-rich fragments  $(\text{CH}_3\text{I})_n\text{CH}_3^+$  ( $n=1-9$ ) at 355 nm excitation is indicative of the ionic-ladder process in which the parent ions are produced directly by absorbing three photons and then dissociates through an additional one-photon absorption to produce fragment ions. These processes are further supported by the laser power dependence of product ions. The results are interpreted in terms of the electronic state diagram of the methyl iodide and effects resulting from intracluster chemical reactions. ©1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Methyl iodide; Multiphoton ionization; Time-of-flight mass spectrometry

### 1. Introduction

The study of chemical reactions in molecular clusters is a rapidly expanding field of research that relies strongly on MPI mass spectrometry for understanding the dissociation mechanism and the dependence of reactivity on cluster size [1–5]. A number of possibilities can be envisioned to describe the mechanism of photoionization and fragmentation in MPI excitation. At any stage of the multiphoton absorption process, the molecule can either absorb another photon (ladder climbing) or dissociate to form a fragment (ladder switching), which in turn can absorb photons and ionize or further dissociate to secondary fragments. The different intermediate excited states can affect the rate of ionization and thus the subsequent ion fragmentation process, possibly due to their unlike excited-state configurations.

Extensive studies of methyl iodide photodissociation have led to important general insights into, e.g., the mechanisms of fragment internal energy disposal, curve crossing, and angular momentum correlation mechanisms [6–9]. The repulsive valence *A* state ( $\sigma^* \leftarrow n$  transition) exhibits a broad

absorption band in the UV centered at  $\lambda_{\text{max}} = 260$  nm. In the VUV the transition to the Rydberg *C* state ( $6p \leftarrow 5p\pi$ ) consists of a sharp series of lines between 200 and 170 nm. The existence of these accessible excited states, which present different photoionization and dissociation dynamics, makes  $\text{CH}_3\text{I}$  an interesting example of polyatomic molecules. Whereas numerous investigations have been reported to differentiate neutral and ionic fragmentation patterns from  $\text{CH}_3\text{I}$  monomer [10–12], there are few reported cases of unraveling the excitation processes and chemical reactions taking place within the clusters.

In this work, we report on the MPI of  $\text{CH}_3\text{I}$  clusters at 266 and 355 nm to investigate the photoexcitation and dissociation channels of  $\text{CH}_3\text{I}$  and to probe how cluster formation affects them. Of particular interest is a comparison of the dissociation dynamics of the methyl iodide clusters at two different excitation processes. The photoreactions are initiated by exciting into the directly dissociative *A* state (266 nm) and the Rydberg *C* state (via 355 two-photon resonance excitation). The fragmentation patterns are discussed in light of the photoexcitation and dissociation dynamics of the intermediate states and the solvation effect of clusters. From the intensity dependence of fragment ions on the laser pulse energy, it is possible to distinguish among the concurrent photochemical processes in  $\text{CH}_3\text{I}$  clusters.

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## 2. Experimental

The apparatus used in our studies has been described in detail in previous publications [13,14]. In brief, it consists of an angular reflectron time-of-flight mass spectrometer used in conjunction with a nanosecond laser system. A carrier gas (ca. 3 atm of He) is bubbled through a reservoir containing the liquid  $\text{CH}_3\text{I}$  (Aldrich, >99.0% pure) at room temperature. The resulting vapor is supersonically expanded through a pulsed nozzle (General Valve) with a 0.5 mm orifice diameter. The neutral clusters pass through a skimmer located 2 cm away from the nozzle and are then ionized by a focused Nd:YAG laser beam (Spectron SL803G). An UV-grade lens of focal length 35 cm was used to focus the laser light into the ionization region of the mass spectrometer. The pulse energy was measured by using a power meter (Moletron PM500D).

The positively charged ions are then accelerated to a normal kinetic energy of 1700 eV through a three plate Wiley–McLaren assembly. The accelerated ions travel through a 1 m long field free region which terminates at a double stage reflectron (R.M. Jordan Co.) located at the end of the flight tube. Following the reflectron, the ions travel an additional 64 cm back to a 40-mm microchannel plate (MCP) detector. The ion signals were averaged by a digital oscilloscope (LeCroy 9350A) normally for 1500 laser pulses at a repetition rate of 10 Hz.

## 3. Results and discussion

Fig. 1 shows a typical TOF mass spectrum observed for a cluster beam of  $\text{CH}_3\text{I}$  at 266 nm. This excitation wavelength lies near the absorption maximum ( $\sim 260$  nm) in the dissociative  $A$  state of  $\text{CH}_3\text{I}$ . The major product ions in the

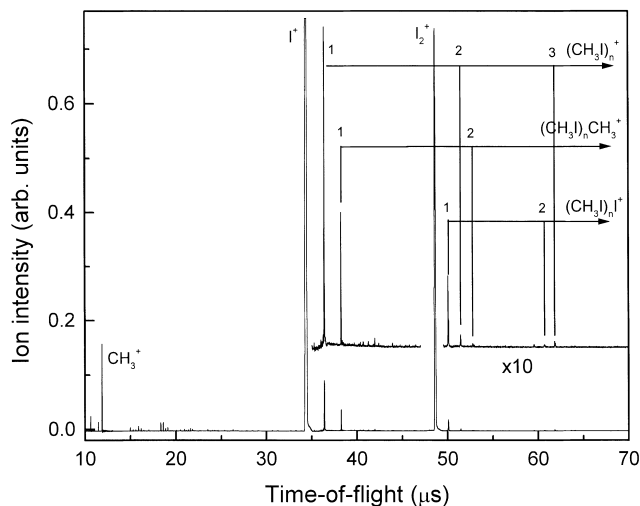


Fig. 1. Multiphoton ionization TOF spectrum of methyl iodide clusters for an excitation wavelength of  $\lambda = 266$  nm. Laser pulse energy is 2 mJ. The expanded signal exhibits the parent and fragment cluster ions.

spectrum are  $\text{CH}_3^+$ ,  $\text{I}^+$ , and  $\text{I}_2^+$ . This is consistent with the previous nanosecond laser MPI experiment [15] on  $\text{CH}_3\text{I}$  monomer at 266 nm, where the major product ions of  $\text{CH}_3^+$  and  $\text{I}^+$  are observed. The dominant  $\text{I}_2^+$  formation is resulted from the neutral cluster reactions and will be described in detail later. In addition, weak ion signals of intact methyl iodide cluster series  $(\text{CH}_3\text{I})_n^+$  ( $n = 1-3$ ), methyl-rich fragments  $(\text{CH}_3\text{I})_n\text{CH}_3^+$  ( $n = 1$  and 2), and iodine-rich fragments  $(\text{CH}_3\text{I})_n\text{I}^+$  ( $n = 1$  and 2) are also observed in the spectrum. The results indicate that at 266 nm excitation, methyl iodide clusters undergo extensive fragmentation as well as evaporation of solvent molecules.

It has been known that the excitation of  $\text{CH}_3\text{I}$  molecule into the repulsive  $A$  state causes a fast C–I bond dissociation into  $\text{CH}_3 + \text{I}$ . Recently, Zewail and co-workers have reported that the dissociation time of  $\text{CH}_3\text{I}$  is found to be 166 fs [16,17]. Since the ionization from the dissociative  $A$  state requires additional two 266 nm photons in the present nanosecond excitation, hence, single-photon dissociation is expected to be strongly favored over ionization as has been demonstrated for picosecond monomer excitation [11,12,18]. Thus significant fragmentation is a consequence of the situation arising from fast dissociation effectively competing with multiphoton ionization of intact  $\text{CH}_3\text{I}$  molecule. The extensive formation of fragment ions is attributed to a ladder-switching mechanism in which the predominant pathway to ions is from one-photon dissociation of  $\text{CH}_3\text{I}$  followed by multiphoton ionization of the neutral  $\text{CH}_3$  and  $\text{I}$  photofragments [15]. It must be presumed that the one-photon photolysis produces an equal number of  $\text{CH}_3$  and  $\text{I}$  fragments, so the small intensity ratio of  $\text{CH}_3^+$  to  $\text{I}^+$  is probably due to the smaller MPI cross section for the  $\text{CH}_3$  radicals than for  $\text{I}$  atoms. The weak signal intensities of cluster ions also support our conclusion that the nanosecond excitation at 266 nm provides an ineffective ionization of unreacted clusters.

The mass spectrum that results from MPI of  $\text{CH}_3\text{I}$  clusters at 355 nm is shown in Fig. 2. The laser pulse energy was 4.0 mJ. Changing the wavelength of the single color ionization laser from 266 to 355 nm affects the fragmentation pattern of these clusters in a significant way, indicating that the excitation process plays an important role on the formation of cluster ions and their ion–molecule reactions within the clusters. Ionization of methyl iodide clusters led to the observation of considerable amount of the parent ion  $\text{CH}_3\text{I}^+$  and its fragments  $\text{CH}_3^+$  and  $\text{I}^+$ . The effective formation of  $\text{CH}_3\text{I}^+$  ions is indicative of direct ionization of  $\text{CH}_3\text{I}$  molecule via multiphoton process. Fragment ions such as  $\text{CH}_3^+$  and  $\text{I}^+$  are thus presumably produced from the dissociative ionization of neutral  $\text{CH}_3\text{I}$  and the photodissociation of  $\text{CH}_3\text{I}^+$  ions by additional photoabsorption.

It is quite interesting to note that at 355 nm methyl-rich  $(\text{CH}_3\text{I})_n\text{CH}_3^+$  ions are predominantly produced among the cluster species. As can be seen in Fig. 2, the mass spectrum contains signals of clusters up to 9-mer. The absorption of the three photons ( $3h\nu = 10.47$  eV) by  $\text{CH}_3\text{I}$  results

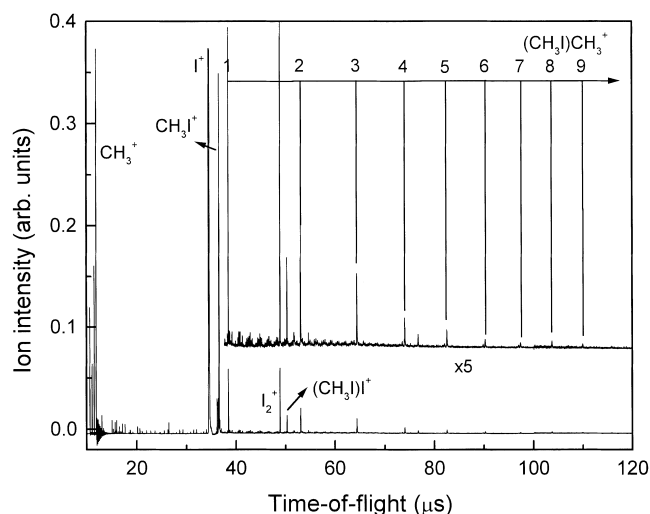
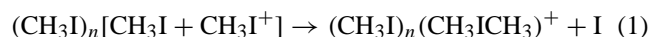
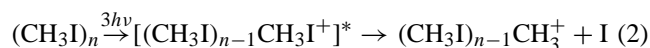


Fig. 2. Multiphoton ionization TOF spectrum of methyl iodide clusters for an excitation wavelength of  $\lambda = 355$  nm. Laser pulse energy is 4 mJ. The expanded signal shows a cluster series of methyl-rich fragment ion.

in formation of  $\text{CH}_3\text{I}^+$  ion (IP=9.538 eV). The resulting parent ion undergoes the intracuster reaction to form the dimethyliodonium ion.

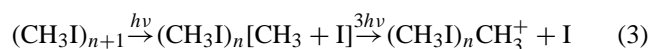


This is in accord with the known ion–molecule chemistry of methyl iodide reported by Beauchamp [19], who observed that  $(\text{CH}_3\text{I})_2\text{I}^+$  is generated by the nucleophilic displacement reaction. Alternatively,  $(\text{CH}_3\text{I})_n\text{CH}_3^+$  formation can be explained by the dissociative ionization of  $\text{CH}_3\text{I}$  clusters within the cluster via three-photon absorption.



The present results strongly demonstrate that at 355 nm the dissociative ionization pathway of  $\text{CH}_3\text{I}^+$  to produce  $\text{CH}_3^+$  ions dominates over  $\text{I}^+$  formation process.

The  $(\text{CH}_3\text{I})_n\text{CH}_3^+$  ions can also be formed from the multiphoton ionization of initially dissociated  $\text{CH}_3$  radicals which do not immediately get ejected.

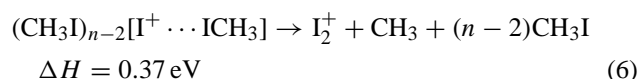
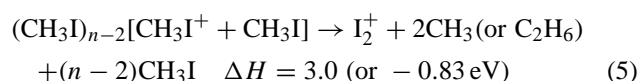
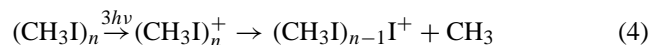


Initial dissociation and sticking of the formed  $\text{CH}_3$  radical to the remaining cluster could account for an enhanced signal of methyl-rich fragments. However, this mechanism seems unlikely since  $\text{CH}_3$  radical contains higher kinetic energy component than I atom, thus easy to be separated from the neighboring molecule.

The observation of  $\text{I}_2^+$  ion in the mass spectrum indicates that chemical reaction occurs inside the clusters since the  $\text{CH}_3^+$ ,  $\text{I}^+$ , and  $\text{CH}_3\text{I}^+$  ions are primarily produced in the MPI mass spectrum of  $\text{CH}_3\text{I}$  monomer at 266 and 355 nm. Sapers et al. first observed  $\text{I}_2^+$  from 248 nm excitation of small  $\text{CH}_3\text{I}$  clusters via time-of-flight mass spectrometry [20]. However, they could not establish the origin of  $\text{I}_2^+$  unambiguously.

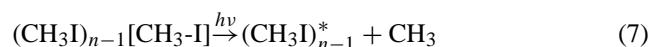
Syage and Steadman [4] have reported picosecond two-color MPI and electron-impact ionization studies of  $\text{CH}_3\text{I}$  clusters at 266 nm. They proposed that, after absorption of one photon by  $\text{CH}_3\text{I}$ , a methyl group is ejected and immediately abstracts a second methyl, forming ethane and  $\text{I}_2$  in a concerted process. The mechanism of  $\text{I}_2^+$  formation is still a matter of controversy.

Based on the present results, there are two classes of possible routes to consider. The first is a multiphoton ionization and fragmentation of  $(\text{CH}_3\text{I})_n^+$  clusters followed by intracluster ion–molecule reactions, which is expected to occur at 355 nm.

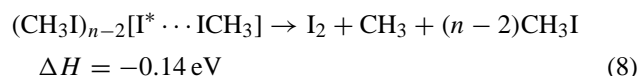


Weak  $\text{I}_2^+$  intensity at 355 nm excitation, in spite of the considerable amount of the observed  $\text{CH}_3\text{I}^+$  ions, indicates that the above reactions do not play an important role in the production of  $\text{I}_2^+$  ions.

The second is a multiphoton ionization of neutral  $\text{I}_2$  product formed from one-photon dissociation of  $\text{CH}_3\text{I}$  molecule and sequential reactions within clusters. At 266 nm, 96% of the absorbing molecules are excited to the  $^3Q_0$  state, which correlates with the  $\text{CH}_3 + \text{I}^*(^2P_{1/2})$  product state [21]. Based on many experiments, it is known that  $\text{I}^*/\text{I}$  branching ratio from the photodissociation of  $\text{CH}_3\text{I}$  in the  $n \rightarrow \sigma^*$  band favors the excited spin-orbit state of I atom [22].

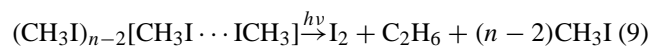


The dissociated I atom in  $(\text{CH}_3\text{I})_n$  photolysis is known to undergo intracluster chemistry leading to  $\text{I}_2$  formation, so the escape of I atom competes with  $\text{I}_2$  formation [23–25].



An additional two-photon absorption ( $2h\nu = 9.32$  eV) by the  $\text{I}_2$  molecule would be required to produce the observed  $\text{I}_2^+$  ions since ionization potential of  $\text{I}_2$  is 9.31 eV [26].

Another possible route for the  $\text{I}_2^+$  formation comes from a concerted photolytic mechanism as proposed recently by Syage [25].



This reaction is exoergic by 0.53 eV assuming a  $(\text{CH}_3\text{I})_n$  binding energy of 0.12 eV [27]. This mechanism is similar to the four-center reactions observed for  $(\text{HI})_2 \rightarrow \text{I}_2 + 2\text{H}$  (or  $\text{H}_2$ ) [28,29]. The  $\text{I}_2$  formation by neutral cluster chemistry

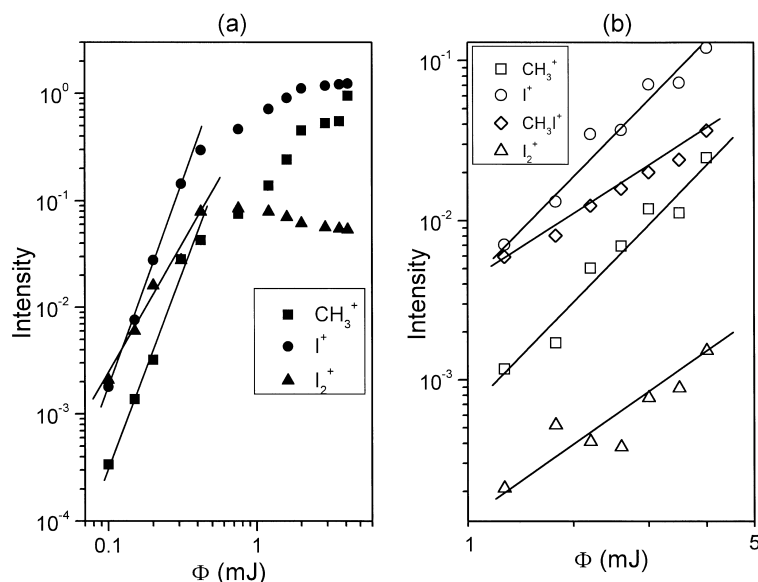


Fig. 3. Plots of the log of ion fragment intensity vs. log of laser pulse energy at (a)  $\lambda = 266$  nm and (b)  $\lambda = 355$  nm. The solid lines are fit to the data.

and its multiphoton ionization is further supported by the observation of dominant  $\text{I}_2^+$  ions at 266 nm rather than at 355 nm.

In order to shed more light on the origin of the ion formation mechanism, we investigated the general trends in the ion abundance distribution of mass spectra as a function of the laser pulse energy,  $\Phi$ . Fig. 3 shows the log–log plots of  $\text{I}^+$ ,  $\text{CH}_3^+$ ,  $\text{CH}_3\text{I}^+$ , and  $\text{I}_2^+$  ion intensities at two different wavelengths. The ion signal of each species is obtained by integration of the corresponding TOF spectrum. At 266 nm, the  $\text{CH}_3^+$  and  $\text{I}^+$  signals vary nonlinearly in the low pulse energies of less than 0.4 mJ and follow 3.7- and 3.6-photon laser intensity dependence, respectively. At higher laser pulse energies, the falling off in the slope provides evidence of saturation.

A four-photon dependence of  $\text{CH}_3^+$  and  $\text{I}^+$  signals at 355 nm is also inferred from the slopes of  $n(\text{CH}_3^+) = 3.9$  and  $n(\text{I}^+) = 3.6$ , within the power range used (1–5 mJ), whereas  $\text{CH}_3\text{I}^+$  increases with third order. The  $\text{I}_2^+$  yields show third order behavior at both excitation wavelengths, indicating that three-photon process is responsible for the  $\text{I}_2^+$  formation, as mentioned above. The decreased intensity of  $\text{I}_2^+$  ions at high laser power (see Fig. 3a) is probably due to their fragmentation into atoms.

The energy diagram of Fig. 4 represents the formation mechanism of neutral fragments and ionic products resulting from photochemistry. Path I is the dissociation of excited neutral  $\text{CH}_3\text{I}$  and subsequent ionization of the dissociation products – ladder switching mechanism. The excitation of  $\text{CH}_3\text{I}$  molecule into the repulsive A state cause the rapid dissociation into  $\text{CH}_3 + \text{I}$  in less than 1 ps. The  $\text{I}^+$  and  $\text{CH}_3^+$  ions formed at low laser power of 266 nm are due to the following processes, as Bernstein et al. [15] have suggested:

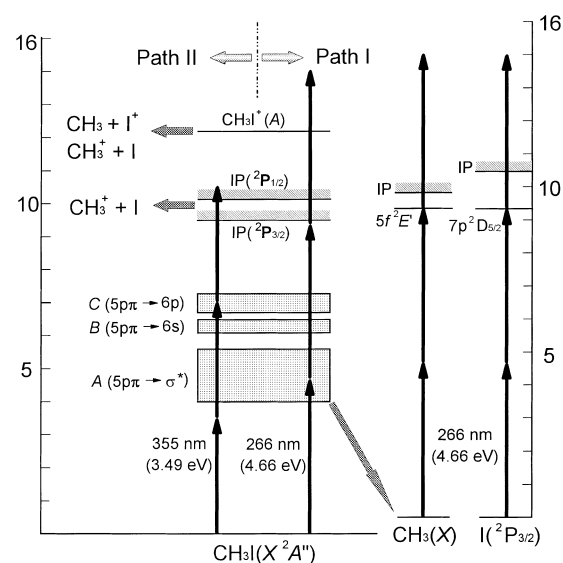
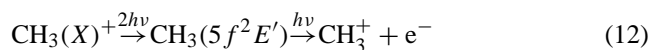


Fig. 4. Scheme of two plausible alternative ionization pathways for the production of parent and fragment ions from  $\text{CH}_3\text{I}$ . The ionization potentials and the appearance potentials shown are taken from refs. [12,30,31]. Path I: Dissociation of the excited  $\text{CH}_3\text{I}$  molecule at 266 nm leads to neutral  $\text{CH}_3$  and  $\text{I}$ . After consecutive photon absorption the fragments are ionized to form  $\text{CH}_3^+$  and  $\text{I}^+$ . Path II: Direct three-photon ionization leads to  $\text{CH}_3\text{I}^+$  and a consecutive photodissociation of  $\text{CH}_3\text{I}^+$  to the fragment ions  $\text{CH}_3^+$  and  $\text{I}^+$ .



At 266 nm, the observed intensities of  $\text{CH}_3^+$  and  $\text{I}^+$  fragments show the fourth order behavior as well as the same increasing tendency with laser pulse energy. These results indicate that the fragment ions are formed through (2+1) photon ionization of neutral  $\text{CH}_3$  and  $\text{I}$  after one-photon dis-

sociation of CH<sub>3</sub>I monomer. Since multiphoton ionization with the 266 nm photons prepares the CH<sub>3</sub><sup>+</sup> and I<sup>+</sup> fragment ions with significant excess energy, it is likely that this excess energy leads to the evaporation of solvating methyl iodide molecules or helium atoms. This would lead to smaller size clusters or even monomer units.

On the other hand, one-photon wavelength of 355 nm does not access any of the excited electronic states. If two-photon resonance enhancement is due to the sharp *C* Rydberg state of the CH<sub>3</sub>I molecule, such a fast dissociation on a femtosecond time scale is not expected. Then the molecular parent ions CH<sub>3</sub>I<sup>+</sup> are expected to be produced via direct three-photon absorption – ladder mechanism (path II). Parker and Bernstein have demonstrated that the electronic excitation processes via two-photon resonance ( $\lambda = 362, 366, 368, \text{ and } 370 \text{ nm}$ ) with different *B*, *C*, and *D* Rydberg states involve the pathway II of Fig. 4 [31]. The ionization process can produce the CH<sub>3</sub>I<sup>+</sup> ion in two spin-orbit components <sup>2</sup>Π<sub>3/2</sub> and <sup>2</sup>Π<sub>1/2</sub> at total ion energies of 9.538 and 10.164 eV, respectively [32]. Absorption of an additional photon would further excite the ion to its dissociative *A* state. Due to the heats of formation of the ions and neutrals under consideration [33] the dissociation of CH<sub>3</sub>I<sup>+</sup> into CH<sub>3</sub><sup>+</sup> or alternatively I<sup>+</sup> is expected to take place after the absorption of a fourth UV photon. A four-photon dependence of CH<sub>3</sub><sup>+</sup> and I<sup>+</sup> ion intensities also support our conclusion that these fragment ions are produced through the one-photon dissociation of CH<sub>3</sub>I<sup>+</sup> ions and their clusters. In addition, it is believed that the effective formation of (CH<sub>3</sub>I)<sub>*n*</sub><sup>+</sup> cluster ions at 355 nm, compared with the results at 266 nm, provides the significant formation of (CH<sub>3</sub>I)<sub>*n*</sub>CH<sub>3</sub><sup>+</sup> ions.

#### 4. Conclusion

The multiphoton ionization and dissociation processes in CH<sub>3</sub>I clusters from 266 and 355 nm have been studied. From the results of mass fragmentation patterns and laser power dependence, it has been possible to clarify the ionization process and photochemical reactions in CH<sub>3</sub>I clusters. At 266 nm, the processes include (a) the one-photon excitation (*A* ← *X*) followed by prompt (<1 ps) dissociation, leading to neutral I/I\* atoms and CH<sub>3</sub> radicals, and (b) two-photon resonant excitation, plus one-photon ionization of I and CH<sub>3</sub>. For  $\lambda = 355 \text{ nm}$  wavelength which shows two-photon resonance with Rydberg *C* state of CH<sub>3</sub>I neutral molecule, the CH<sub>3</sub><sup>+</sup> and I<sup>+</sup> ions are produced from dissociation of the CH<sub>3</sub>I<sup>+</sup> parent ion rather than from the multiphoton ionization of the dissociation products of the excited methyl iodide. The reactions responsible for the formation of I<sub>2</sub><sup>+</sup> ions at 266 nm are likely confined to the neutral, rather than ionic, photochemistry within the clusters.

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